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LCA OF CHEMICALS

Attributional life cycle assessment (ALCA) of polyitaconic acid production from northeast US softwood biomass

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Abstract
Purpose Shifting the resource base for chemical and energy production from fossil feed stocks to renewable raw materials is seen by many as one of the key strategies towards sustainable development. The objective of this study is to assess the environmental burdens of producing polyitaconic acid (PIA), a water-soluble polymer derived from itaconic acid identified by the US Department of Energy as one of the top 12 value added chemicals from northeast (NE) US softwood biomass. Results are compared to corn-derived PIA and fossil-based poly acrylic acid (PAA) on the basis of 1 kg of polymer at the factory gate.
Methods This study uses attributional life cycle assessment to quantify global warming potential (GWP), fossil energy demand (CED), acidification, eutrophication, water use, and land occupation of the polymer production routes. This includes feedstock growth and harvest, sugar extraction, fermentation, itaconic acid recovery, and subsequent polymerization. Foreground data for softwood-derived PIA comes from lab- and pilot plant runs undertaken by Itaconix LLC.
Results and discussion Results indicate that the use of softwood-based PIA may be advantageous in terms of GWP, CED, and acidification when compared to both, the integrated corn biorefinery and fossil-based PAA production. When looking at impacts to eutrophication and water use, the use of softwood leads to lower potential impacts compared to its corn-based counterpart but to higher impacts when compared to fossil-based PAA. Land occupation, to a large extent, due to lower yields and longer growth cycles associated with softwood growth in the NE, is highest for softwood-derived PIA and lowest for fossil-based PAA. Environmental impacts are mainly the results of onsite electricity use, inputs of activated carbon and sodium hydroxide, as well as water use during sugar extraction and fermentation. Assumptions with regards to allocation, activated carbon inputs, and electricity mixes to processes of the foreground system are tested in a sensitivity analysis.
Conclusions Wood-derived PIA production may be an interesting alternative to current fossil-based pathways and could contribute to a future biobased economy. However, currently, land occupation, water use, and eutrophication are high when compared to traditional PAA production. The use of short rotation crops or waste feedstocks and optimization with regards to water requirements and reuse should be investigated to further lower system-wide impacts.

Keywords Biopolymers · Corn feedstock · Integrated biorefinery · Life cycle assessment (LCA) · Polyacrylic acid · Polyitaconic acid · Softwood biomass · Stream-integrated process

1 Introduction

The last decade has seen a strong political and technical focus on using biomass feedstock to produce biofuels and energy. Much less attention has been given to biomass as a feedstock for chemicals production (Dodds and Gross 2007). However, while the economy of energy can be based on various alternative technologies utilizing, e.g., wind, sun, and water, the materials economy of substances will increasingly depend on the use of renewable biomass as well as the reutilization of existing material stocks within the

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technosphere. Using biomass to generate electricity and process heat is likely to be a bridge technology before other renewable energy becomes economically viable on a widespread basis. It is expected that as the era of a chemical industry, based on nonrenewable oil and gas, will gradually come to an end over the course of the next 50–75 years, industrial production of platform chemicals from biomass feedstock will become of growing interest (Kamm et al. 2006).

In 2004, itaconic acid (IA) was identified by the US Department of Energy–Energy Efficiency and Renewable Energy as one of the top 12 value added chemicals potentially available from biomass (Werpy and Petersen 2004). After polymerization, biobased polyitaconic acid (PIA) may functionally be an alternative to fossil-derived polyacrylic acid (PAA), a well-established petrochemical with a current global production of more than two million tons per year (Itaconix, LLC 2009). PIA is a water-soluble polymer with a wide range of possible applications including super-absorbents, anti-scaling agents in water treatments, co-builders in detergents, and dispersants for minerals in coatings (Itaconix, LLC 2009). PIA is currently produced from corn-derived IA by fermentation. The use of woody biomass from the northeastern (NE) USA as feedstock for PIA production is investigated by Itaconix LLC[1] via a *stream-integrated approach* in which extracted softwood hemicellulose serves as feedstock for PIA production, while the partially macerated wood and lignin can still be used in other existing processes such as pulp and paper plants for conventional pulp and bioenergy production (Durant, personal communication; Itaconix, LLC 2009).

The seven states of the NE USA[2] have abundant forest resources and an established forest management sector (Benjamin et al. 2009). Currently, the region has an average accessible forestland cover of 70.6 %, ranging from a high of 88.4 % in Maine to a low of 52.8 % in Rhode Island (Benjamin et al. 2009; US Forest Service 2010). The total accessible forestland area totals 49.9 million acres. For new biorefineries to work in a competitive manner, the degree to which existing feedstock use overlaps with biomass requirements for new biochemical production pathways needs to be examined. The stream-integrated approach proposed may offer advantages in terms of feedstock competition. However, it is unclear if the use of wood-derived feedstock for PIA production is beneficial from an environmental perspective.

[1] www.itaconix.com

[2] Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island, and Vermont

2 Methods

Against this background, the purpose of this paper is to assess the cradle-to-gate environmental burdens associated with softwood-derived PIA production and how these compare to conventional production practices. The study uses *attributional life cycle assessment* in combination with commonly used impact assessment (LCIA) methods to evaluate mid-point impacts to *global warming potential* (GWP) and *cumulative energy demand* (Goedkoop et al. 2008), *acidification* and *eutrophication* (Bare et al. 2002), as well as *water use* and *land occupation* (Goedkoop et al. 2009). Impacts to acidification and eutrophication are based on (Bare et al. 2002), as their LCIA method applies region-specific characterization factors more in line with the geographical scope (USA) of our assessment. In addition, we include ReCiPe end-point impacts (H/A v1.05; Goedkoop et al. 2009) in our analysis to provide complementary single-score results for each production pathway for easier comparison. However, due to the uncertainties associated with end-point calculations, these results should only be interpreted in conjunction with midpoint impacts provided. *SimaPro 7.3* is used to build the LCA model and carry out the impact assessment.

2.1 Functional unit and system boundary

The synthesis pathway assessed in this report produces *Itaconix™ Dispersant DSP2K* (poly(sodium itaconate)), a low molecular weight linear polyitaconic acid partially neutralized with sodium salt (Itaconix, LLC 2010). In the present study, for simplicity the product is assumed to be functionally equivalent to fossil-based poly(sodium acrylate) which is obtained by polymerizing acrylic acid partially neutralized with sodium salt. We assume that PIA (DSP2K) based on either woody biomass or corn feedstock has similar or better properties in comparison to its fossil-based counterpart and would *functionally substitute* poly (sodium acrylate). Hence, a *functional unit* of 1 kg of dry polymer is used. For the remainder of this paper we will use the abbreviation *PIA* for the poly(sodium itaconate) product and *PAA* for the poly (sodium acrylate) product.

Figure 1 shows the major stages of the product systems, which are investigated as unit processes. The system under consideration includes wood cultivation and harvest, transport to the biorefinery, hemicellulose (xylane) extraction, fermentation, recovery of the IA, and polymerization into PIA. The hemicellulose extraction process yields valuable by-products including Kraft pulp (macerated wood) and lignin that can be used in conventional pulp and paper mills. We assume the *diversion* of hemicellulose to the PIA biorefinery, while under current practices both hemicellulose and lignin (present as "black liquor" during the Kraft

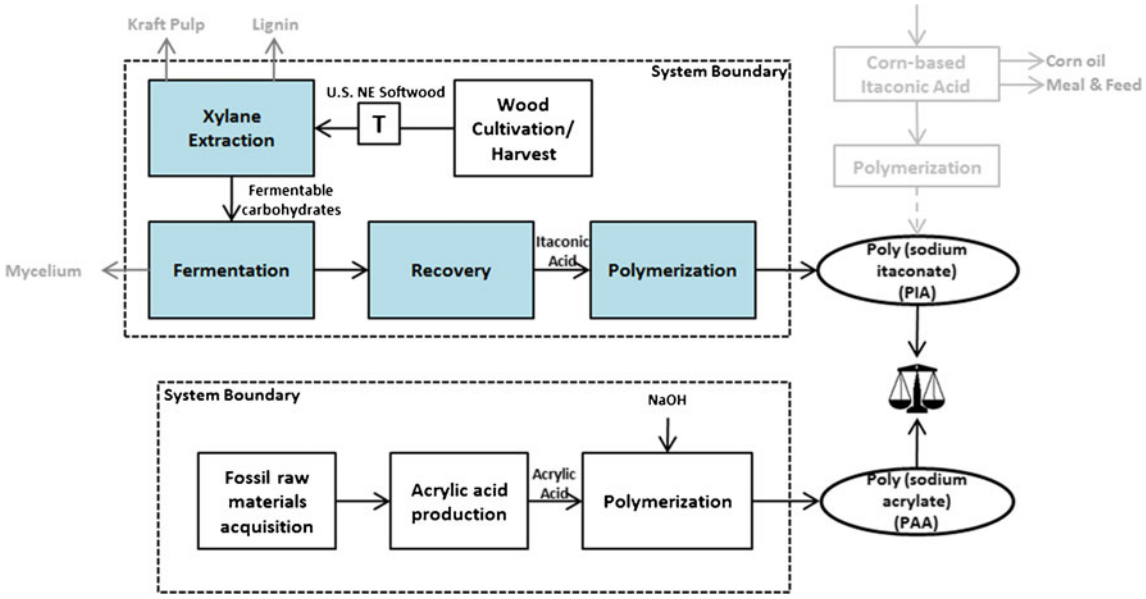

Fig. 1 System boundary of the PIA production route studied

process) are used mostly for energy recovery on site of the pulp and paper plant. Fermentation yields mycelium as by-product which could serve as protein-rich animal feed after drying. For multi-output processes, *mass allocation* is applied. The impact of *economic allocation* on results is tested in a sensitivity analysis.

Results are compared to PIA produced from corn-based IA. The life-cycle includes corn cultivation and harvest and transportation to the biorefinery, corn wet milling, and fermentation into IA followed by polymerization using the Itaconix process. Furthermore, the life cycle of functionally equivalent PAA consists of fossil raw materials acquisition, acrylic acid production via the acrolein process (two-step propylene oxidation), polymerization, and neutralization using sodium hydroxide (NaOH).

2.2 Biogenic carbon accounting

We do not include biogenic CO_2 emissions from cellular respiration during fermentation in impacts to GWP. Furthermore, carbon dynamics associated with forest growth (see, e.g., (Johnson 2009; McKechnie et al. 2011; Walker 2010)) are excluded from the analysis. In addition, datasets used for corn production in the USA (Ecoinvent 2010; Jungbluth et al. 2007) do not include carbon emissions from indirect land use change which may be an important contributor to GWP.

During PIA production, carbon present in the hemicellulose (from softwood) or glucose (from corn) feedstocks will be: (1) respired as CO_2 during fermentation, (2) incorporated into the mycelium byproduct, and (3) incorporated into the final PIA polymer. PIA, e.g., used in detergents and dispersants would presumably have a short life time (days to months) before biodegradation takes place and carbon would therefore not be captured over longer time periods (i.e., years as in durable goods such as certain plastics). The duration over which carbon storage occurs will hence depend on the type of polymer use and consumer habits. PIA synthesis will store 1.45 kg CO_2/kg PIA based on the chemical formula for PIA sodium salt (*Itaconix DSP2K*), $(C5H5O4.Na)_x$. We report impacts to GWP both including and excluding carbon temporarily sequestered in the PIA polymer. Including carbon sequestration may be justified in products such as diapers with lifetimes of months to years, considering that under current practices most of the hemicellulose would be burned together with lignin (black liquor) to recover energy (hence immediately releasing carbon to the atmosphere).

2.3 Life cycle inventory

Data for the biorefinery unit processes (see Fig. 1) is based on *confidential process data* from Itaconix and its partners (Durant, personal communication). It should be noted that with the exception of the polymerization step, the data used for softwood-based PIA production stems from lab- and pilot-plant test runs and was assumed to be scalable to larger operations (see also Section 4.2). Inputs of materials, energy, and resource use are modeled using data from the Ecoinvent (2010) and US Life Cycle Inventory (LCI) database (NREL 2008). The modeled biorefinery is located in the US NE region with biomass feedstock (softwood or

corn) available within a 70 m radius.[3] The NE power grid distribution (NEPOOL; ISO New England 2010) is used for electricity inputs to the unit processes. We test the sensitivity of results with regards to varying power grid inputs to biorefinery unit processes, i.e., NEPOOL (ISO New England 2010), US average (Ecoinvent 2010), and hydropower (Bauer et al. 2007; Ecoinvent 2010). The following sections explain process steps and assumptions in more detail. Due to the confidentiality of some of the foreground data obtained directly from Itaconix (Durant, personal communication), quantitative numbers are only partly provided.

2.3.1 Softwood-based PIA

The softwood-derived PIA production system is divided into five major steps including (1) softwood cultivation and harvest; (2) transport of softwood to the xylane extraction plant followed by wood processing and conversion into fermentable carbohydrates (mainly xylose); (3) conversion of carbohydrates into IA via fermentation; (4) recovery of the acid as sodium itaconate; and (5) conversion of sodium itaconate into poly(sodium itaconate) (DSP2K) polymer.

Softwood growth and harvest Significant differences between countries and even regions within the USA (e.g., NE USA vs. Inland Northwest) exist in terms of site preparation activities, stand establishment, and fertilization (Oneil et al. 2010). For instance, for the NE no slash reduction activities are mandated for wildfire risk reduction, natural forest regeneration is assumed to be sufficient on all sites with no need for fertilization. In contrast, forest management activities in the northwestern USA generally include seedling production for regrowth, commercial thinning, and fertilization. We use the datasets for softwood growth and harvest and subsequent conversion towards sawlogs and pulplogs from (NREL 2008; Oneil et al. 2010).[4] We consider pulpwood from forest harvest as feedstock for the integrated biorefinery. Wood chipping takes place by feeding the softwood logs at forest road into a mobile chopper (Ecoinvent 2010). With 4.05 m3/hayear (Oneil et al. 2010), land occupation associated with NE softwood provision compares to a US country average net annual increment (NAI)[5] of 3.64 m3/hayear (Smith et al. 2009). Data on urban land occupation associated with forest roads comes from Werner et al. (2007). *Allocation* of environmental burdens is *based on* the *weight* of pulpwood and by-products (i.e., sawlogs and bark).

Xylane extraction Softwood chips are transported to the conversion plant from within a 70 m radius using a truck (NREL 2008). Wood chips are continuously fed to the extraction column and hemicelluloses xylane polymers extracted using steam. Steam is provided to the process from a natural gas (36.6 MJ/kg PIA) fired steam boiler located on site (Durant, personal communication). Electricity (0.56 kWh/kg PIA) is required to power auxiliary process equipment (e.g., conveyor belt and water pumps) (Durant, personal communication). The extraction process yields *fermentable carbohydrates* (7 % dry weight), *lignin* (1 %), and *pulp-grade wood* (92 %). Lignin and partially macerated (pulp grade) wood are separated from the liquid extract. Activated carbon (AC; obtained from charcoal (Ecoinvent 2010) and activated using excess steam from the hemicellulose extraction process) and ionic exchange columns are used to remove potential fermentation inhibitors (e.g., acid soluble lignin or furfural) from the liquid extract before it is diverted to the fermenter. A total of 67.1 kg softwood chips at a moisture content of 55 % are required for the production of 1 kg PIA and by-products[6] (before allocation). The diversion of (hemicellulose derived) fermentable carbohydrates is accounted for by *mass as well as economic allocation* based on the economic heating value of each product output (Section 3.1 of Electronic supplementary material (ESM)). Based on a heating value of 13.6 MJ/kg for hemicellulose and 25 MJ/kg for lignin (Amidon 2006), and a heating value of 15 MJ/kg and market price of $35/ton for pulp-grade wood (Durant, personal communication), the economic value of hemicellulose and lignin equals $32/ton and $59/ton, respectively.

Fermentation IA is produced by fermentation of xylose and other extracted carbohydrates received from the wood extraction unit (referred to only as xylose throughout this paper). The process combines xylose and other media, adds a microbial inoculum as well as micronutrients to fuel the fermentation process, and produces crude IA (Durant, personal communication). Electricity (1.16 kWh/kg PIA) is used to power an air compressor and separation unit, adjusting fermentation conditions and controlling foam built-up and micronutrients added (Durant, personal communication). The outputs of the fermentation process are a clarified broth containing *IA* as well as *mycelium* from fungus growth. The culture broth is filtered to remove mycelia and other suspended solids. *Allocation* of environmental burdens is *based on* the dry *weight* of the product outputs.

[3] In reality, the corn-based biorefinery would likely be located in the Midwestern USA in close proximity to the corn belt. However, since the goal and scope of this paper is to compare the biorefinery process using wood to the use of corn, we choose similar electricity mixes for all processes of the foreground system.

[4] The process "Pulpwood, softwood, US NE-NC" is used.

[5] NAI represents the average annual volume over a reference period of gross increment less natural losses and hence represents a good estimate for the required forest land area for biomass provision.

[6] This includes pulp-grade wood, lignin, and mycelium.

We investigate the impact of *economic allocation* (sensitivity analysis) using a current average market price of $1.63/kg[7] for IA (Itaconix, LLC 2009) and $0.80/kg for mycelium assumed to replace high-protein soybean animal feed (USDA 2011; Section 3.1 of ESM).

Recovery After fermentation, IA is extracted from the clarified and filtered broth solution. Regeneration of the extractant solution (0.13 kWh/kg PIA) is required (Itaconix, LLC 2009). NaOH pellets (0.26 kg/kg PIA) are added to adjust the pH of the solution and AC added to further purify the broth before concentration using an evaporator takes place (Durant, personal communication). The main output of the recovery process step is an evaporated solution containing *sodium itaconate* (NaIA). Due to a lack of data on the detailed composition of *wastewater* generated, we use typical numbers from commercial polylactic acid (PLA) production according to Althaus et al. (2007a, b) and Vink et al. (2003, 2007).

Polymerization Polymerization is based on a method developed by Itaconix that eliminates the need for post polymerization purification. An initiator is added to the itaconate solution to start the polymerization reaction (Durant, personal communication). The conversion efficiency is high and the resulting polymer is further packaged as a granulated material.

2.3.2 Corn-based PIA

Corn-based PIA represents a potential competitive alternative to wood-derived PIA (ESM Fig. S1). The LCI for corn-based PIA is based on a combination of data describing (1) Corn production in the USA (including farm equipment use; Ecoinvent 2010; Jungbluth et al. 2007); (2) glucose production via corn wet milling (Akiyama et al. 2003; Gerngross 1999; Khoo et al. 2010; US EPA 2011); and (3) fermentation, IA recovery, and polymerization (Durant, personal communication). The PIA production plant is located on site the wet mill and hence no transportation of glucose is required. About 1.46 kg corn is required to produce 1 kg of glucose (Akiyama et al. 2003). By-products of the process are 0.378 kg corn meal and feed as well as 0.063 kg corn oil (allocation is based on mass). The energy requirements are estimated to be 4.9 MJ/kg glucose (corn wet milling). The transportation distance of corn to the biorefinery is assumed to equal 49.5 m one way (corn basket with a radius of 70 m[8]) via a combination truck using US average fuel (NREL 2008). The input of dry glucose to the fermentation process is 1.71 kg/kg of PIA produced (Durant, personal communication). Yields, resource, and energy inputs as well as emissions associated with fermentation, recovery, and polymerization are assumed to be similar to wood-based PIA production (see previous section). We account for water requirements for subsequent fermentation. In order to be in line with ecoprofiles on biopolymers published elsewhere (Vink et al. 2003, 2007, 2010) enzyme use (0.1 % by weight of corn input) is included in the assessment. However, due to a lack of LCI data on industrial enzyme production for integrated corn refineries, it was decided to use data on fungal glucoamylase production (Nielsen et al. 2006) as a proxy for environmental burdens.

2.3.3 Fossil-based PAA

PAA is produced from fossil-derived acrylic acid via polymerization using a radical initiator. Acrylic acid is produced via a two-step process from propylene. Due to limited process data publically available on industrial PAA production, we use data from ecoinvent (Althaus et al. 2007a, b) on acrylic acid production. In order to allow a fair comparison with PIA produced via the Itaconix process, we account for NaOH inputs required for the generation of sodium acrylate. We assume that the polymerization step of PIA and PAA production is not significantly different and use data on yields, energy requirements, and amount of initiator used from (Durant, personal communication). Polymerization takes place in water using roughly 1 kg of process water per kilogram of polymer generated (Durant, personal communication). The final product is 1 kg of dry poly(sodium acrylate) at the factory gate.

3 Results and discussion

3.1 Midpoint Impacts

Table 1 shows quantitative results of the comparative LCA looking each at 1 kg softwood- and corn-derived PIA as well as fossil-based PAA. Relative contributions of process steps to each impact category are shown in Section 2.1 of ESM.

Results indicate that with 1.32 kg CO_2-eq per kilogram product output (or −0.13 kg CO_2-eq if the carbon temporarily sequestered in PIA is included), the wood-based polymer has a significantly lower *GWP* than both corn-based PIA (2.19 or 0.74 kg CO_2-eq if the carbon sequestered in PIA is included) as well as fossil-based PAA (2.74 kg CO_2-eq; ESM Fig. S2). Polymerization, with its high conversion efficiency, contributes only a minimal

[7] This price is simply based on currently existing commercial IA production pathways and does not imply the production cost or target price for Itaconix LLC.

[8] Given a radius of 70 m, the transportation distance was calculated as follows:

$$1 \Big/ \sqrt{2} \cdot 70\ miles = 49.5\ miles.$$

Table 1 Results of the comparative LCA for all six impact categories investigated

Impact category	Unit PIA	Wood PIA	Corn PAA	Fossil-based
GWP 100a	kg CO2 eq	1.32	2.19	2.74
		−0.13[a]	0.74[a]	–
CED (fossil/nuclear)	MJ eq	14.99	24.80	70.58
Acidification	H+ moles eq	0.378	0.726	0.453
Eutrophication	kg N eq	0.009659	0.016420	0.000425
Water use	m^3	0.007506	0.012290	0.004784
Land occupation	m^2a	8.412	2.457	0.024

The functional unit for comparison is 1 kg of polymer at the factory gate. Land occupation for the wood-derived polymer is mainly due to the use of forest land (NE pulpwood used as PIA feedstock; woody biomass used for AC provision), while corn-based PIA requires both agricultural (corn feedstock) and forest land area (AC provision)

[a] Including the carbon temporarily sequestered in the PIA polymer (1.45 kg CO_2-eq)

share to overall GWP, while IA recovery from the broth solution leads to roughly 0.92 kg CO_2-eq for both biobased polymers (wood and corn). The reason for this is mainly the use of NaOH, used for neutralization and formation of NaIA, and AC added before evaporation takes place. In addition, electricity required during fermentation and IA recovery contributes to GWP. The major difference between the wood- and corn-based production routes in terms of CO_2 emissions are the different contributions of feedstock growth/harvest as well as sugar extraction. The production of a unit of fermentable sugars (xylose and others) from softwood biomass from the northeast leads to a lower GWP than the provisions of a unit of glucose from corn feedstock via corn wet milling for subsequent PIA production. This trend is visible throughout the various impact categories, except for impacts to land occupation (see below).

With 15.0 MJ-eq, the wood-based route requires significantly less primary and secondary *energy* from fossil and nuclear sources[9] than corn-based PIA (24.8 MJ-eq) and their fossil-based counterpart (70.6 MJ-eq[10]). Trends observed are similar to GWP (ESM Fig. S3). The reason is that the energy content of the biomass feedstock (softwood or corn) is not captured in the indicator. However, even if we account for fossil energy demand (CED) including renewables such as biomass and others, the environmental burdens are still lower than for PIA from corn and fossil-based PAA (ESM Fig. S4).

Acidification associated with corn-based PIA production is with 0.73 H^+ moles-eq almost twice as high as for wood-based PIA (0.38 H^+ moles-eq) and fossil-based PAA (0.45 H^+ moles-eq; ESM Fig. S5). The unit processes leading to the highest share in acidification burdens for the corn-based route are electricity inputs to corn wet milling and glucose fermentation process (51 %) as well as NaOH inputs to the recovery step (27 %) and corn production (22 %), during which, e.g., ammonia and nitrous oxides from fertilization are emitted to the environment.

Eutrophication is highest for the corn-based production route (0.0164 kgN-eq) and lowest for fossil-based PAA (0.00043 kgN-eq; ESM Fig. S6). The reason for this is that during IA recovery, large amounts of wastewater are generating causing eutrophication during conventional treatment (Ecoinvent 2010). Due to a lack of site-specific wastewater composition data, we use numbers for commercial PLA production (Werner et al. 2007) and therefore the eutrophication potential should only be seen as a first indicator. For corn-based PIA, corn growth and harvest lead to additional eutrophication impacts (0.00669 kgN-eq) mainly due to commercial fertilizer use. In contrast, according to Oneil et al. (2010), softwood production in the NE USA generally does not use any fertilizer during the growth phase[11] and therefore eutrophication impacts are minimal. However, this assumption will differ depending on forest management practices and whether future demands can be supplied from naturally regenerating forests in the NE.

Impacts to *water use* are caused mainly by water use during feedstock growth (irrigation) and inputs to the biorefinery, in particular to the unit processes of fermentable sugar extraction and fermentation (ESM Fig. S7). With 0.0123 m^3/kg PIA, water use seems highest for the corn-based route, followed by 0.00751 m^3/kg for wood-based PIA and 0.00478 m^3/kg for conventional PAA. Corn feedstock irrigation results in 0.0047 m^3 of water use, while NE softwood stems from naturally grown forests not requiring artificial irrigation. Corn wet milling and fermentation lead to an additional demand of 0.0017 and 0.0051 m^3 water,

[9] The CED indicator encompasses nonrenewable fossil (i.e., coal, oil, etc.) and nuclear (i.e., uranium) energy demand.

[10] Includes fossil feedstock energy.

[11] According to Oneil et al. (2010), fertilization is used by a few large private landowners but it is overall not a common practice in the NE region.

respectively. For the softwood-based polymer, impacts to water use are a result mostly of water used for xylane extraction and fermentation, wastewater treatment, and AC production (background process).

The production of wood-derived PIA leads to the occupation of 8.3 m^2a forest and 0.092 m^2a urban land area (ESM Fig. S8). *Land occupation* is to 77 % due to softwood tree growth, which have relatively long rotation cycles (65 years) and lower yields per hectare and year when compared to corn feedstock. This is due to the fact that NE forest biomass comes from naturally regenerating forests (i.e., no short rotation plantations are used). The use of pulpwood from naturally regenerating forest in the NE USA has to be distinguished from the use of feedstock grown on agricultural land (e.g., corn feedstock) specifically for the purpose of use in a biorefinery. Both may result in different pressures on ecosystems per unit of land area occupied. The remaining 23 % of land occupation are due to land requirements for AC provision (produced from hardwood residuals) used during IA recovery. Urban land occupation is small (by a factor of 100) when compared to forest land and is mainly due to the use of forest road for vehicles to access forest area for maintenance and final harvest (Werner et al. 2007). No infrastructure area requirements for the biorefinery plant are accounted for.

With 2.4 m^2a of land used (roughly 25 % of this is due to agricultural land occupation for corn production and 75 % due to charcoal (AC) production from forest lands), the use of corn seems beneficial from a land occupation standpoint when compared to softwood-based PIA production (ESM Fig. S8). The share of urban land occupation is negligible. However, the diversion of pulp softwood towards PIA production on scales that would allow continued sustainable forestry practices (i.e., harvest in NE forests equals natural regeneration) would also help to preserve NE forest lands. Hence, the occupation of naturally regenerating forest land may have positive aspects that are only captured by extending the analysis to investigate related ecosystem pressures per square meter of land occupied, and by including land transformation in the analysis (see, e.g., Koellner and Scholz 2007). This remains to be done in a future study. In contrast to both biobased polymers, fossil-based PAA production (a highly optimized process) results in significantly less land occupation (0.0244 m^2a/kg) since mostly fossil feedstock (crude oil for the generation of propylene) is required.

3.2 Endpoint impacts (ReCiPe World H/A)

Endpoint impacts using the ReCiPe World H/A method (Goedkoop et al. 2009) indicate that the softwood-based production route results in lower environmental burdens when compared to PIA derived from corn and PAA obtained from fossil resources (Fig. 2). Relative contributions to each process step of wood-based PIA production can be found in ESM Fig. S9.

3.3 Sensitivity analysis (see Section 3 of ESM)

Applying *economic allocation* instead of mass allocation to the biorefinery model (sugar extraction and fermentation) leads to a slight increase of environmental burdens for both PIA production routes (Section 3.1 of ESM). The reason is that IA obtained from fermentation has a high market price when compared to mycelium (assumed to serve as high-protein animal feed). In contrast to this, applying economic values to the products of the sugar extraction process does not significantly change allocation percentages. However, even if economic allocation is applied to both unit processes (sugar extraction and fermentation), impacts to GWP (1.46 or 0.01 kg CO_2-eq if the carbon temporarily sequestered in the PIA is included), CED (17.3 MJ-eq), and acidification (0.433 H^+moles-eq) for the softwood-based route are still significantly lower when compared to corn-based PIA (2.66 kg CO_2-eq (or 1.21 kg CO_2-eq if the carbon temporarily sequestered in the polymer is included), 31.0 MJ-eq, 0.914 H^+moles-eq), and fossil-based PAA (2.74 kg CO_2-eq, 70.6 MJ-eq, 0.423 H^+moles-eq) production.

Replacing the NEPOOL power mix with *hydropower* reduces GWP for the softwood-based polymer to 0.96 kg CO_2-eq (−0.49 kg CO_2-eq if the carbon sequestered in the PIA is included), CED to 9.4 MJ-eq, and acidification to 0.232 H^+moles-eq (Section 3.2 of ESM). Impacts to eutrophication, water use, and land occupation are mainly a result of direct inputs and/or emissions to the biorefinery system including feedstock growth/harvest. As a result, these impacts are less influenced by choices made with regards to the electricity inputs. Overall, using hydropower has the potential to reduce impacts to all categories (reductions in eutrophication and land occupation are minimal), while using US average power would lead to the highest impacts to all categories. For corn-based PIA, a similar tendency is observed.

AC used for the removal of chemical substances from the broth solution (sugar extraction and fermentation) was assumed to be disposed of after use (i.e., burned on site without energy recovery). In reality, AC in stacks may be reactivated using heat (e.g., provided by burning by-products from extraction on site). In addition, the amount of AC is likely to vary depending on the final process design and concentration of chemical substances to be removed. Varying the amounts of AC from the baseline configuration (100 %) to half (50 %) and twice (200 %) the amount of AC, respectively, most significantly impacts GWP as well as land occupation (Section 3.3 of ESM). For example,

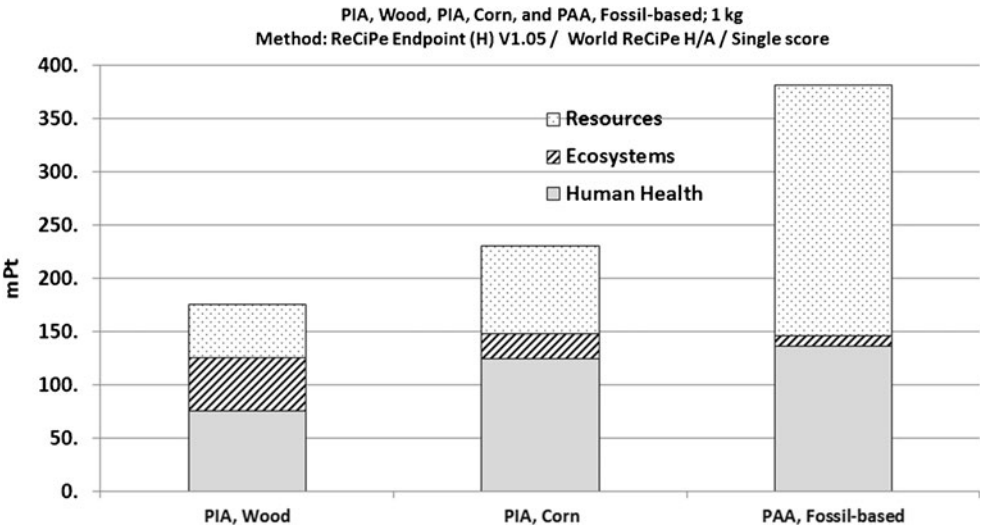

Fig. 2 Comparison of endpoint impacts (ReCiPe World H/A v1.05) associated with 1 kg of PIA production from softwood and corn and in comparison to conventional fossil-based PAA (biogenic carbon temporarily sequestered in PIA is not included in this figure). It should be noted that calculation of a single score leads to higher uncertainty when compared to midpoint indicators. The result should therefore be used in connection with midpoint results (see previous sections)

reducing overall AC use by half could lead to a reduction of roughly 17 % in GWP for the softwood-based biorefinery (1.32–1.09 kg CO_2-eq[12]) and 10 % for the corn-based route (2.19–1.98 kg CO_2-eq[13]). Similarly, land occupation could be reduced by 11 % from 8.4 to 7.5 m^2a/kg for softwood-based PIA and 38 % from 2.5 to 1.5 m^2a/kg for corn-based PIA, respectively.

4 Conclusions

4.1 Recommendations

Among the main contributors to both wood and corn-based PIA production are: (1) *electricity used during fermentation and IA recovery*, (2) *AC used during IA recovery and sugar extraction (only for wood-based PIA)*, (3) *NaOH used during recovery*, (4) *water use during sugar extraction and fermentation*, and (5) *land occupation associated with softwood, corn, and AC inputs*. As a result, life cycle wide systems performance is directly affected by variations in these inputs.

For example, the choice of a less carbon intensive *electricity mix* (e.g., from hydropower) on site the biorefinery could be combined with increased energy efficiency measures, i.e., optimizing the electricity inputs in particular to air compression (fermentation) and evaporation/concentration (IA recovery). Furthermore, lowering *AC* inputs to the unit processes of extraction and recovery (e.g., by regeneration on site) may contribute to reduce impacts in particular to GWP and land occupation. The use of *NaOH* most significantly contributes to GWP, CED, and acidification. This is due to upstream burdens associated with NaCl production and power use in the diaphragm membrane and cell electrolysis processes. NaOH is used up by the process and therefore needs to be continuously replaced. System-wide impacts with regards to NaOH are unlikely to be reduced as the neutralizing agent is part of the final polymer product and is likely to be the simplest neutralizing agent available. *Water use* for sugar extraction and subsequent fermentation may be reduced by investigating onsite effluent treatment and enhanced recirculation (e.g., of distilled water obtained during evaporation). High water use may be an obstacle for PIA production in arid regions. Finally, considering short-rotation plantations and waste feedstocks (e.g., softwood derived from forest residuals, construction, and demolition waste, etc.) could help to reduce impacts to land occupation.

4.2 Limitations of the LCA

Attributional LCA Results of the LCA describe the environmentally relevant flows using *current inventory data* and market prices for economic allocation. However, many of the assumptions made in this assessment might change over time. For example, market prices used for economic allocation fluctuate on a daily basis, in particular with regards to global prices for, e.g., corn and other food crops. The LCA model does not consider changes in other parts of the economy that may be due to, e.g., the diversion of wood- or corn-based feedstock to PIA production. This type of analysis does therefore not take into account that due to a decision supported by the LCA, production patterns might be changed in the future.

Cradle-to-gate perspective Our assessment does not include the use and disposal phase of the polymer product. PIA and PAA polymers can be used in a variety of applications (e.g., superabsorbents, antiscaling agents in water treatment, co-builders in detergents, etc.) and all of these products will

[12] From −0.13 to −0.36 kg CO_2-eq if the carbon temporarily sequestered in the PIA is included.
[13] From 0.74 to 0.53 kg CO_2-eq if the carbon temporarily sequestered in the PIA is included.

have different use phases, lifetimes, and disposal scenarios. By choosing a *cradle-to-gate* perspective, these environmental impacts are not included in our assessment.

Forest growth carbon dynamics A distinction is made between fossil and biogenic sources of carbon emitted to the atmosphere. Biomass feedstock for PIA production is assumed to be carbon neutral. However, there is a recent controversy among the scientific community with regards to the carbon neutrality of biomass (Johnson 2009). Literature published on the subject suggests to report carbon stock changes and to include the effect of time in any sustainability analysis (Johnson 2009; McKechnie et al. 2011; Walker 2010). Especially in temperate forests, in which the harvest cycle can range from 60 to 100 or more year, carbon stock replacement can take many decades. We did not account for carbon dynamics associated with forest growth as this was outside the goal and scope of the assessment.

Geographical scope of the assessment The study has been carried out for NE USA using region-specific data for softwood growth, the NEPOOL power mix, and US-specific LCIA characterization factors for acidification and eutrophication (Bare et al. 2002). Forest growth and harvest practices in NE USA are distinctively different from other regions. For example, no artificial fertilization of the trees is undertaken and rotation age and harvest yields were found to be significantly different than for other regions. Therefore, results of the study may not directly be applied to other regions of the USA or the world.

Lab- and pilot-scale data Finally, the life cycle inventory compiled for this assessment is based on preliminary energy and mass balances from Itaconix and its partners (Durant, personal communication). *Data comes from lab- and pilot plant test runs* and was assumed to be scalable to larger facilities. In reality, some of the data used in our assessment might change for a commercial facility. In addition, the process might be further optimized in the future according to experience gained during commercial operation.

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References

Akiyama M, Tsuge T, Doi Y (2003) Environmental life cycle comparison of polyhydroxyalkanoates produced from renewable carbon resources by bacterial fermentation. Polym Degrad Stabil 80 (1):183–194

Althaus H-J, Hischier R, Osses M, Primas A, Hellweg S, Jungbluth N, Chudacoff M (2007a) Life cycle inventories of chemicals data v2.0. Ecoinvent Centre. ETH Zurich, Dübendorf

Althaus H-J, Werner F, Stettler C (2007b) Life cycle inventories of renewable materials data v2.0. Ecoinvent Centre. ETH Zurich, Dübendorf

Amidon TE (2006) The biorefinery in New York: woody biomass into commercial ethanol. Pulp Pap-Can 6(107):47–50

Bare JC, Norris GA, Pennington D, McKone T (2002) Traci—the tool for the reduction and assessment of chemical and other environmental impacts. J Ind Ecol 6(3–4):49–78

Bauer C, Bolliger R, Tuchschmidt M, Faist-Emmenegger M (2007) "Wasserkraft." Sachbilanzen von energiesystemen: grundlagen fuer den oekologischen Vergleich von Energiesystemen und den Einbezug von Energiesystemen in Oekoblianzen fuer die Schweiz, Ecoinvent Report No. 6-VIII (In German), R. Dones, ed., Paul Scherrer Institute Villigen, Swiss Centre for Life Cycle Inventories, Dübendorf, Switzerlan

Benjamin J, Lilieholm RJ, Damery D (2009) Challenges and opportunities for the northeastern forest bioindustry. J For 107(3):125–131

Dodds DR, Gross RA (2007) Chemistry: chemicals from biomass. Science 318(5854):1250–1251

Ecoinvent (2010) Ecoinvent life cycle inventory database v2.2. Swiss Centre for Life Cycle Inventories

US Forest Service (2010) Forest Inventory and Analysis National Program—tools and data. http://www.fia.fs.fed.us/tools-data/default.asp. Accessed on: 27 Dec 2010

Gerngross TU (1999) Can biotechnology move us towards a sustainable society. Nat Biotechnol 17:541–544

Goedkoop M, Oele M, de Schryver A, Vieira M (2008) SimaPro database manual—methods library. PRé Consultants, Netherlands

Goedkoop M, Heijungs R, Huijbregts M, De Schryver A, Struijs J, Van Zelm R (2009) ReCiPe 2008, a life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level; First edition Report I: Characterisation. (www.lcia-recipe.net)

Itaconix, LLC (2009) The development of integrated production of polyitaconic acid from Northeast hardwood biomass. Grant Project Proposal, Itaconix, LLC, (Principal); Microbia, Inc.; University of Maine

Itaconix, LLC (2010) Technical datasheet: ITACONIX™ Dispersant DSP2K

Johnson E (2009) Goodbye to carbon neutral: getting biomass footprints right. Environ Impact Assess 29(3):165–168

Jungbluth N, Chudacoff M, Dauriat A, Dinkel F, Doka G, Emmenegger MF, Gnansounou E, Kljun N, Schleiss K, Spielmann M, Stettler C, Sutter J (2007) Life cycle inventories of bioenergy. Ecoinvent report no.17. Swiss Centre for Life Cycle Inventories, Dübendorf

Kamm B, Gruber PR, Kamm M (2006) Biorefineries—industrial processes and products: status quo and future directions, volume 2. Wiley, New York

Khoo HH, Tan RBH, Chang KWL (2010) Environmental impacts of conventional plastic and bio-based carrier bags. Int J Life Cycle Assess 15(3):284–293

Koellner T, Scholz R (2007) Int J Life Cycle Assess 12(1):16–23

McKechnie J, Colombo S, Chen J, Mabee W, MacLean HL (2011) Forest bioenergy or forest carbon? Assessing trade-offs in greenhouse gas mitigation with wood-based fuels. Environ Sci Technol 45(2):789–795

ISO New England (2010) 2010 Regional System Plan (www.iso-ne.com)

Nielsen PH, Oxenbøll KM, Wenzel H (2006) Cradle-to-gate environmental assessment of enzyme products produced industrially in denmark by novozymes A/S. Int J Life Cycle Assess 12(6):432–438

NREL (2008) U.S. Life Cycle Inventory Database (U.S. LCI), v1.6.0. National Renewable Energy Laboratory (NREL)

Oneil EE, Johnson LR, Lippke BR, McCarter JB, McDill ME, Roth PA (2010) Life-cycle impacts of Inland Northwest and Northeast/North Central Forest Resources. 42(CORRIM Special Issue), pp. 29–51

Smith WB, Miles PD, Perry CH, Pugh SA (2009) Forest Resources of the United States, 2007. Gen. Tech. Rep. WO-78. U.S. Department of Agriculture, Forest Service, Washington Office, Washington, p 336

US EPA (2011) Chapter 9: food and agricultural industries, AP 42, fifth edition, volume I. Office of Air Quality Planning and Standards

USDA (2011) Agricultural marketing service—market news and transportation data. http://www.ams.usda.gov/AMSv1.0/ams.fetchTemplateData.do?startIndex=1&template=TemplateW&page=SearchFeedstuffsReports. 6 Jul 2011

Vink ETH, Rábago KR, Glassner DA, Gruber PR (2003) Applications of life cycle assessment to NatureWorks(TM) polylactide (PLA) production. Polym Degrad Stabil 80(3):403–419

Vink ETH, Glassner D, Kolstad J, Wooley R, O'Connor R (2007) The eco-profiles for current and near-future NatureWorks® polylactide (PLA) production. Ind Biotechnol 3(1):58–81

Vink ETH, Davies S, Kolstad J (2010) The eco-profile for current Ingeo® polylactide production. Ind Biotechnol 6(4):212–224

Walker T (2010) Massachusetts Biomass Sustainability and Carbon Policy Study: report to the Commonwealth of Massachusetts Department of Energy Resources. Natural Capital Initiative Report. Manomet Center for Conservation Science, Brunswick

Werner F, Althaus H-J, Kuenninger T, Richter K, Jungbluth N (2007) Life cycle inventories of wood as fuel and construction material—data v2.0. Dübendorf: Switzerland

Werpy T, Petersen G (2004) Top value added chemicals from biomass, volume 1: results of screening for potential candidates from sugars and synthesis gas. National Renewable Energy Laboratory (NREL) and Pacific Northwest National Laboratory (PNNL)